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| <b>(54) Title:</b> FIBER-REINFORCED SYNTACTIC FOAM COMPOSITES AND METHOD OF FORMING SAME<br><br><b>(57) Abstract</b><br><br>Fiber-reinforced syntactic foam composites having a low specific gravity and a low coefficient of thermal expansion suitable for forming lightweight structures for spacecraft applications are prepared from a mixture of a heat curable thermosetting resin, hollow microspheres having a diameter of about 5 to 200 micrometers and fibers having a length less than or equal to 250 micrometers.   |           |  |

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FIBER-REINFORCED SYNTACTIC  
FOAM COMPOSITES  
AND METHOD OF FORMING SAME

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BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates, in general, to syntactic foam composites and, more particularly, to fiber-reinforced thermosetting resin based syntactic foam composites exhibiting a low specific gravity and a low coefficient of thermal expansion.

10

2. Description of the Prior Art

A continuing objective in the development of satellites is to optimize satellite payload weight. One means of achieving this objective is to reduce the intrinsic weight of various operational elements within the spacecraft. It has been recognized by the art that the desired weight reduction could be realized by replacing conventional materials, such as aluminum, with lower density synthetic composites possessing requisite mechanical, thermal and chemical stability. 15 Included in these low density synthetic composites is a group of materials referred to in the art as syntactic foams. 20

1           Syntactic foams are produced by dispersing  
microscopic rigid, hollow or solid particles in a  
liquid or semi-liquid thermosetting resin and then  
hardening the system by curing. The particles are  
5           generally spheres or microballoons of carbon, polystyrene,  
phenolic resin, urea-formaldehyde resin, glass, or  
silica, ranging from 20 to 200 micrometers in diameter.  
Commercial microspheres have specific gravities ranging  
from 0.033 to 0.33 for hollow spheres and up to 2.3 for  
10          solid glass spheres. The liquid resins used are the  
usual resins used in molding reinforced articles, e.g.,  
epoxy resin, polyesters, and urea-formaldehyde resins.

          In order to form such foams, the resin containing  
a curing agent therefor, and microspheres may be mixed  
15          to form a paste which is then cast into the desired  
shape and cured to form the foam. The latter method,  
as well as other known methods for forming syntactic  
foams, is described by Puterman et al in the publication  
entitled "Syntactic Foams I. Preparation, Structure,  
20          and Properties," in the Journal of Cellular Plastics,  
July/August 1980, pages 223-229. When fabricated in  
large-block form, such foams possess a compressive  
strength which has made them suitable for use in submerged  
structures. In addition, the more pliable versions of  
25          the foam are utilized as filler materials which, after  
hardening, function as a machinable, local-densification  
substance in applications such as automobile repair and  
the filling of structural honeycombs. Despite these  
characteristics of adequate compressive strength, good  
30          machineability, and light weight, such foams lack the  
degree of dimensional and thermal stability required to  
render them applicable for the spacecraft environment.  
More specifically, syntactic foam systems tend to  
exhibit varying filler orientation and distributions  
35          within the geometrical areas in a molded intricate  
structure, which limits the structural intricacy that

1 can be achieved, as well as reducing dimensional  
stability. If syntactic foam systems are too highly  
filled, sacrifices are made in moldability, coefficient  
of thermal expansion, strength, density, dimensional  
5 stability and stiffness. Moreover, such foams tend to  
exhibit poor adhesion to metallic plating which is  
required to form the desired product, such as an antenna  
component.

10 In order for the syntactic foam to be useful  
as a substitute for aluminum in antenna and antenna  
microwave components in a spacecraft, the foam must  
have the following characteristics.

15 (1) The material must have a specific gravity  
of 1.00 or less, as compared to a specific gravity  
of 2.7 for aluminum.

20 (2) The material must have a linear coefficient  
of thermal expansion ( $\alpha$  or CTE) comparable  
to that of aluminum, preferably close to  
 $13 \times 10^{-6}$  in/in/°F ( $23 \times 10^{-6}$  cm/cm/°C) or less.  
Thermal distortion of antenna components subjected  
to thermal cycling in the extremes of the space  
environment is a major contributing factor to  
gain loss, pointing errors, and phase shifts.

25 (3) The material must meet the National  
Aeronautics and Space Administration (NASA)  
outgassing requirements to insure that the  
material does not release gaseous component  
substances which undesirably accumulate on other  
spacecraft parts in the outer-space vacuum.

30 (4) The material must have long-term  
stability, as required for parts exposed to the  
space temperature environment (e.g., -100°F to  
250°F or -73°C to 121°C) for extended periods of  
time, such as 10 years.

1           (5) The material must be capable of being  
cast into complex configurations in order to form  
component parts for antenna structures, such as  
waveguides or antenna feed distribution networks.

5           The art, until the present invention, has been  
unable to satisfy these requirements and particularly the  
requirement for a low coefficient of thermal expansion  
( $\alpha$ ). Thus, known epoxy resin based syntactic foams filled  
with 10 to 30% by volume hollow microspheres generally  
10 have a  $\alpha$  in the range of  $17$  to  $36 \times 10^{-6}$  in/in/°F  
( $30$  to  $65 \times 10^{-6}$  cm/cm/°C).

A need, unsatisfied by existing technology, has  
thus developed for a syntactic foam material which is  
both lightweight and of sufficient mechanical, thermal  
15 and chemical stability to enable it to be substituted  
for aluminum in physically demanding satellite  
environments.

#### SUMMARY OF THE INVENTION

20           The unresolved needs of the art are satisfied by  
the present invention which provides thermally stable  
fiber-reinforced syntactic foam composites having a  
specific gravity of less than 1.0 and a linear coefficient  
of thermal expansion of about  $25 \times 10^{-6}$  in/in/°F  
25 ( $45 \times 10^{-6}$  cm/cm/°C) or less, which are prepared from  
an admixture of a heat curable thermosetting resin,  
hollow microspheres having a diameter between about 5  
and about 200 micrometers and fibers having a length of  
about 50 to about 250 micrometers.

30           The syntactic foam composites of the present  
invention can be cast as complex structures which  
contain lightweight hollow microspheres having fibers,  
such as graphite fibers, in the voids between the  
microspheres, with the microspheres and fibers being  
35

1 bonded together by the heat cured resin matrix. The  
composites of the present invention readily meet the  
specific gravity, coefficient of thermal expansion and  
NASA outgassing requirements, which easily qualify the  
5 composites as aluminum substitutes for spacecraft use.

#### DETAILED DESCRIPTION OF THE INVENTION

10 In order to form the fiber-resin-microsphere  
composite of the present invention having the desired  
density and coefficient of thermal expansion, each of  
the three components must be selected so that the  
resulting combination thereof provides a mixture amenable  
to being cast into the desired configuration, as well  
as providing a final product having the required  
15 structural and physical properties. Acceptable mixtures  
must have a viscosity that produces an accurate, void-  
free casting with uniform material properties. In  
addition, the proportion of fiber in the composite must  
provide the required thermal expansion, strength, and  
20 stiffness properties. Further, the microsphere component  
must be chosen to provide the required low density in  
the composite. Finally, each of the components must be  
capable of being combined with the other components and  
the effect of each on the other in the mixture thereof,  
25 as well as in the final composite must be taken into  
account. In particular the properties of the composite  
are influenced by the properties, relative volume  
ratios, and interactions of the individual components.  
More specifically, density, strength, stiffness  
30 (brittleness), coefficient of thermal expansion and  
processibility are strong functions of filler and fiber  
type, volume ratios and micropacking. The following  
discussion provides a more detailed consideration of  
these various factors. It should be noted that in the

1 following discussion, the term "syntactic foam" is used  
herein to denote a filled polymer made by dispersing  
rigid, microscopic particles in a fluid polymer or  
resin and then curing the resin, as is known in the  
5 art. The term "fiber-reinforced syntactic foam composite"  
is used herein to denote the cured product formed from  
the mixture of resin, microballoons, and reinforcing  
fibers in accordance with the present invention.

10 1. Heat Curable Resin

The heat curable, thermosetting resins used to  
prepare the syntactic foam composites of the present  
invention can be any heat curable thermosetting resin  
having appropriate viscosity for casting (e.g., less  
15 than 1000 centipoise), pot life (e.g., greater than 2  
hours), coefficient of thermal expansion, and thermal  
stability in the temperature range of -100°F to 250°F  
(-73°C to 121°C) required in the space environment.  
The resin material contains a curing agent which reacts  
20 with the resin to produce a hardened material. Curing  
agents and other additives will, of course affect the  
viscosity and other properties of the final mixture  
from which the composite is formed. Examples of suitable  
resins include low viscosity, polymerizable liquid  
25 polyester resins which comprise the product of the  
reaction of at least one polymerizable ethylenically  
unsaturated polycarboxylic acid, such as maleic acid or  
its anhydride, and a polyhydric alcohol, such as, for  
example, propylene glycol and optionally, one or more  
30 saturated polycarboxylic acids, such as, for example,  
phthalic acid or its anhydride. Other suitable resins  
include condensates of formaldehyde such as urea-  
formaldehyde, melamine-formaldehyde and phenol-  
formaldehyde resins. Preferred resins for use in the

35



1 practice of the present invention are epoxy resins  
having 1,2 epoxy groups or mixtures of such resins,  
and include cycloaliphatic epoxy resins such as the  
glycidyl ethers of polyphenols, liquid Bisphenol-A  
5 diglycidyl ether epoxy resins (such as those sold  
under the trademarks Epon 815, Epon 825, Epon 828 by  
Shell Chemical Company), phenolformaldehyde novolac  
polyglycidyl ether epoxy resins (such as those sold  
under the trademarks DEN 431, DEN 438 and DEN 439 by  
10 Dow Chemical Company), and epoxy cresol novolacs (such  
as those sold under the trademarks ECN 1235, ECN 1273,  
ECN 1280 and ECN 1299 by Ciba Products Company).

The particular epoxy resins preferred in the  
practice of the present invention are polyglycidyl  
15 aromatic amines, i.e. N-glycidyl amino compounds prepared  
by reacting a halohydrin such as epichlorohydrin with  
an amine. Examples of the most preferred polyglycidyl  
aromatic amines include diglycidylaniline, diglycidyl  
orthotoluidine, tetraglycidyl ether of methylene dianiline  
20 and tetraglycidyl metaxylene diamine, or mixtures  
thereof.

The epoxy resins which are preferably in liquid  
form at room temperature are admixed with polyfunctional  
curing agents to provide heat curable epoxy resins  
25 which are cross-linkable at a moderate temperature,  
e.g., about 100°C, to form thermoset articles. Suitable  
polyfunctional curing agents for epoxy resins include  
aliphatic polyamines of which diethylene triamine and  
triethylene tetramine are exemplary; aromatic amines of  
30 which methylene dianiline, meta phenylene diamine,  
4,4' diaminodiphenyl sulfone are exemplary; and  
polycarboxylic acid anhydrides of which pyromellitic  
dianhydride, benzophenone tetracarboxylic dianhydride,  
hexahydrophthalic anhydride, nadic methyl anhydride  
35 (maleic anhydride adduct of methyl cyclopentadiene),

1 methyl tetrahydrophthalic anhydride and methyl  
hexahydrophthalic anhydride are exemplary. Polycarboxylic  
acid anhydride compounds are preferred curing agents  
for the above-noted preferred epoxy resins, with the  
5 three compounds last noted being most preferred.

In preparing heat curable, thermosetting, epoxy  
resins compositions, the epoxy resin is mixed with the  
curing agent in proportions from about 0.6 to about 1.0  
of the stoichiometric proportions, which provides suffi-  
10 cient anhydride groups and carboxylic acid groups to react  
with from about 60 to 90 percent of the epoxide groups.  
The term "curing" as used herein denotes the conversion  
of the thermosetting resin into an insoluble and infusible  
cross-linked product and, in particular, as a rule,  
15 with simultaneous molding to give shaped articles.

In addition curing accelerators may be added to  
the epoxy resins, as is known in the art, to provide a  
low curing temperature. Preferred accelerators for the  
above-noted preferred polyglycidyl aromatic amine  
20 resins are substituted imidazoles, such as 2-ethyl-4-  
methyl imidazole, and organometallic compounds, such as  
stannous octoate, cobalt octoate, and dibutyl tin  
dilaurate which are incorporated at a concentration of  
zero to about 3 parts by weight per 100 parts resin.

25 Moreover, other materials may be added to the  
epoxy material in order to improve certain properties  
thereof, as is known in the art. For example, the  
tendency of the resin to separate from the mixture  
can be minimized by the addition of fine particulate  
30 fillers, such as Cab-O-Sil (a fumed silica manufactured  
by Cabot Corporation), acicular fibers, such as talc,  
or short chopped or milled fibers. In addition, resin  
penetration of the filler may be enhanced by the addition  
of a titanate wetting, agent, such as KR38S, an isopropyl  
35 tri(dioctylpyrophosphate) titanate, available from  
Kenrich Petrochemical Co.

1           A particularly useful resin composition for  
forming the composites of the present invention comprises  
a polyglycidyl aromatic amine, a polycarboxylic acid  
anhydride curing agent, and a curing accelerator.  
5       Examples 3 and 4 herein are directed to the use of  
this preferred resin formulation in the practice of  
the present invention.

## 2. Hollow Microspheres

10           The syntactic foam composites prepared in accordance  
with the present invention contain a relatively uniform  
distribution of hollow microspheres. These hollow  
microspheres are usually hollow thermoplastic spheres  
composed of acrylic-type resins such as polymethyl-  
15       methacrylate, acrylic modified styrene, polyvinylidene  
chloride or copolymers of styrene and methyl methacrylate;  
phenolic resins; or hollow glass, silica or carbon spheres  
that are very light in weight and act as a lightweight  
filler in the syntactic foam. These microspheres  
20       preferably have a diameter in the range of about 5 to  
about 200 micrometers. Methods for the production of  
these hollow microspheres are well known in the art  
and are discussed, for example, by Harry S. Katz and  
John V. Milewski in the book entitled, "Handbook of  
25       Fillers and Reinforcements for Plastics," Chapter 19:  
Hollow Spherical Fillers, Van Nostrand Reinhold, 1978,  
the teachings of which are incorporated herein by  
reference. Such microspheres are readily available  
commercially. These hollow microspheres can be  
30       compressed somewhat when subjected to external pressure.

1       However, they are relatively fragile and will collapse  
or fracture at high pressures. Therefore, there is a  
pressure range under which the microspheres can  
effectively operate. It has been determined that when  
5       hollow glass microspheres are employed in the practice  
of the present invention, syntactic foam composites  
can be molded at pressures up to the limit of the  
hollow microspheres without fracture, with molding  
pressures in the range of about 700 to about 900 psi  
10       (0.102 to 0.131 pascals) being preferred.

By controlling the amount of hollow microspheres  
added to the syntactic foam, it is possible to control  
the specific gravity of the foam. A simple mixture of  
an epoxy material and hollow microspheres tends to  
15       separate on standing, with the microballoons rising to  
the surface of the epoxy. However, it has been found  
that with an increased volume of microballoons added  
to the epoxy, there is a decreased tendency to separate  
into discrete phases. Moreover, it has been found  
20       that at a sufficiently high loading of microballoons,  
namely about 65% by volume for microballoons, the  
tendency to separate into discrete phases is minimized.  
To achieve specific gravities of less than 1.0, the  
hollow microspheres are included in the syntactic foam  
25       in up to 65% by volume and generally in a range of  
about 35 to about 65% by volume and preferably about  
50 to about 65% by volume. The volume percentage of  
hollow microspheres is adjusted based on the composition  
of the hollow microsphere selected, the brand of micro-  
30       spheres and the size of the microspheres. Therefore,  
it may be necessary to select the proper mixture of  
heat curable resin material and hollow microspheres  
for preparation of the syntactic foam on a trial and  
error basis. For example, the C15/250 series of glass  
35       microspheres available from the 3M Company has a specific  
gravity of 0.15 and a mean diameter of 50 micrometers.

1 "Carbosphere" carbon microspheres available from the  
Versar Corporation have a specific gravity of 0.32 and  
a mean diameter of 50 micrometers. Desirably, a mixture  
of two or more types of hollow microspheres may be  
5 employed in the practice of the present invention. The  
glass microspheres provide the syntactic foam with  
improved structural strength, while those of carbon  
advantageously contribute to both a lowered coefficient  
of thermal expansion and greater amenability to subsequent  
10 metal-plating operations. When using a combination of  
glass and carbon microspheres in preparing the composites  
of the present invention, the ratio of glass microspheres  
to carbon microspheres is about 1:4 to 1:1.

Furthermore, it has been found by using packing  
15 theory that an increased volume percent solids in the  
resin mixture can be achieved. Packing theory is based  
on the concept that, since the largest particle size  
filler in a particular reinforcement system packs to  
produce the gross volume of the system, the addition of  
20 succeeding smaller particles can be done in such a  
way as to simply occupy the voids between the larger  
filler without expanding the total volume. This theory  
is discussed by Harry S. Katz and John V. Milewski, in  
the book entitled "Handbook of Fillers and Reinforcements  
25 for Plastics," Chapter 4. Packing Concepts in Utilization  
of Filler and Reinforcement Combinations, Van Nostrand  
Reinhold, 1978. The fillers used in the present  
invention are chosen on the basis of particle size,  
shape, and contribution to overall composite properties.  
30 This theory applies to the use of solid particulates as  
well as hollow spheres. Because of the high viscosity  
of such a highly loaded resin, the mixture could not  
flow into the mold without damaging the microspheres.

1 To overcome this problem, the mold is pre-packed with  
the dry filler (i.e. a mixture of microspheres and  
fibers). By applying packing theory as described above,  
the filler can be packed at high density and so that  
5 segregation of ingredients does not occur.

Finally, the microspheres may be advantageously  
treated with a coupling and wetting agent to enable the  
resin to wet the sphere surfaces and promote good filler-  
resin adhesion, as discussed in greater detail below  
10 with regard to similar treatment of the fibers used in  
the present invention.

### 3. Fibers

The fibers used in the practice of the present  
15 invention must be compatible with the selected resin in  
order to provide good coupling between the fiber and  
resin. Fibers such as graphite, glass, Kevlar (an  
aromatic polyamide material obtained from E. I. Dupont  
and Company) nylon, or carbon are added to the syntactic  
20 foam composite of the present invention to improve the  
strength and dimensional stability of the composite.  
However, the contribution of the fiber to the coefficient  
of thermal expansion of the composite product and to  
the viscosity of the mixture of components must also  
25 be considered. Graphite fibers have been found to be  
particularly useful since they provide the desired  
strength in the composite, while also reducing the  
coefficient of expansion of the composite. An additional  
factor to consider is fiber length. While shorter  
30 fibers (e.g. having a length-to-diameter ratio of less  
than 100:1) provide less reinforcement per fiber than  
do longer fibers, shorter fibers have less impact on  
the viscosity of the mixture. Thus, a greater volume  
fraction of shorter fibers can be incorporated into a

1 mixture at a given level of viscosity, which provides a  
higher level of reinforcement at that viscosity level  
by shorter fibers. In addition, the use of shorter  
5 fibers improves the uniformity of the mix. Thus,  
fibers useful in the composite of the present invention  
have a length less than or equal to 250 micrometers  
and generally in the range of about 50 to about 250  
micrometers. Fibers having a length about 150 to  
10 about 250 micrometers were found to provide the best  
compromise between viscosity and reinforcement as  
discussed previously. When graphite fiber, the preferred  
fiber material, is used, the diameter of the graphite  
fibers is in the range of about 5 to about 10 micrometers.

Moreover, the interaction of the fibers with the  
15 microspheres discussed previously must be considered.

It has been determined by micropacking theory, as  
described in Chapter 4 of the book by Katz and Milewski,  
previously referenced, that the optimum ratio of fibers-  
to-spheres varies with the length/diameter ratio ( $L/D$ )  
20 of the fibers and with the ratio of the sphere-diameter  
to the fiber-diameter ( $R$ ). For each value of  $L/D$ ,  
there is one  $R$  value where the packing efficiency is  
zero; and as  $R$  increases or decreases on either side of  
this minimum, packing efficiency increases. It has  
25 been found most desirable in the practice of the present  
invention to use graphite fibers of the micrometer  
lengths discussed above, which have a length to diameter  
ratio ( $L/D$ ) of about 5:1 to about 30:1 and preferably  
about 15:1 to about 30:1, and a sphere-diameter to  
30 fiber-diameter ratio ( $R$ ) of at least about 6:1 and  
preferably about 15:1.

Graphite fibers used in the practice of the  
present invention are selected to have high strength  
and low density. Celanese GY-70 graphite fiber and  
35 Courtaulds HM-S graphite fiber are especially suitable.

1 Celanese GY-70 fiber is 8 micrometers in diameter,  
has a tensile strength of 76,000 pounds per square inch  
( $3.6389 \times 10^6$  Pa), a specific gravity of  $1.83 \text{ gm/cm}^3$   
and an  $\alpha$  of  $-0.3 \times 10^{-6} \text{ in/in/}^\circ\text{F}$ . Courtaulds HM-S  
5 graphite fibers have a diameter of 8 micrometers, a  
tensile strength of 50,000 psi ( $2.394 \times 10^6$  Pa), a  
specific gravity of  $1.91 \text{ gm/cm}^3$  and a longitudinal  
 $\alpha$  of  $-1 \times 10^{-6} \text{ in/in/}^\circ\text{F}$ . The graphite fibers are  
commercially available as continuous-fiber tows. For  
10 example, Celanese GY-70 fiber consists of 384 fibers/tow.  
The fiber tows are reducible to required lengths on the  
order of between about 50 micrometers and 250 micrometers  
by ball milling or from commercial processing concerns  
such as the Courtaulds Company of the United Kingdom.

15 The amount of fiber incorporated in the resin-  
microsphere admixture generally ranges from about 3 to  
about 10 volume percent and preferably from about 3 to  
about 5 volume percent in order to achieve composites  
having  $\alpha$  values of  $25 \times 10^{-6} \text{ in/in/}^\circ\text{F}$  ( $45 \times 10^{-6} \text{ cm/cm/}^\circ\text{C}$ )  
20 or less.

As the amount of hollow microspheres and fibers  
incorporated in the heat curable resin increases, there  
is a corresponding increase in the viscosity of the  
resin. High viscosity prevents uniform dispersion of  
25 the microspheres and fibers and interferes with the  
processing of the resin-microsphere-fiber mixture during  
molding operations. However, in order to reduce the  
viscosity of the mixture, the surfaces of the microspheres  
and fibers may be provided with a thin layer of coupling  
and wetting agents. The microsphere and fiber surfaces  
30 are treated with a solution containing a silane coupling  
agent such as Silane A-186 (beta(-3,4-epoxy cyclohexyl)-  
ethyltrimethoxy silane), Silane A-1120 (n-beta-  
(aminoethyl)-gamma-aminopropyl tri-methoxy-silane) or a  
35



1 titanate coupling agent such as di(dioctylpyrophos-  
phato)ethylene titanate (KR238M available from Kenrich  
Petrochemical Company of Bayonne, New Jersey); or  
5 tetra(2,2 diallyloxymethyl-1-butoxy)titanium di(ditridecyl  
phosphite) (KR55 available from Kenrich); or titanium  
di(cumylphenylate) oxyacetate (KR134S available from  
Kenrich); or isopropyl tridodecylbenzenesulfonyl  
(KR9S available from Kenrich). The coupling agents  
10 enable the resin to wet the sphere and fiber surfaces, and  
promote a stronger bond between the resin, microspheres,  
and fibers without increasing the viscosity appreciably.

The coupling agents may be applied by simply  
dissolving the agents in the resin-microsphere-fiber  
blend. Optionally, these agents may be applied by  
15 first dissolving the agents at a concentration of  
0.1 - 0.5% of the filler weight in water or an organic  
solvent such as isopropanol or Freon TE (a fluorocarbon  
compound available from E.I. Dupont and Company); and  
then immersing the microspheres and fibers which have  
20 been premixed in predetermined proportions in the  
solution for a period of 5 to 30 minutes, followed by  
filtering and drying the mixture. The microsphere-fiber  
mixture may then be blended with the heat curable resin  
preparatory to fabricating the syntactic foam composite.

#### 25 4. Optional Microbeads

Solid microbeads may optionally be incorporated  
in the composite of the present invention in order to  
increase packing efficiency. Advantageously, such  
30 microbeads were also found to decrease the viscosity of  
the formulation, improve its pourability, and increase  
composite uniformity. In a preferred practice of the  
present invention, about 2 to about 8 percent by volume  
of solid inert material, such as glass or silica micro-  
35 beads having a diameter of about 2 to about 8 micrometers

1 and a specific gravity of 2.2 to 2.4 are incorporated  
in the resin-microsphere-fiber admixture. Volume  
percentages in excess of 8% increase the viscosity of  
the uncured, filled heat curable resin formulation to  
5 a level at which it is unworkable for molding purposes.  
In addition, it was found that large filler volume  
fractions (volume of microballoons, fiber and microbeads  
greater than 60 percent) had a reduced coefficient of  
thermal expansion, but the viscosity of the mix was  
10 unworkable. Small volume fractions of filler (i.e.  
volume of microballoons, fiber, and microbeads less  
than 40 percent) were found to improve processability,  
but increased the coefficient of thermal expansion to  
an unacceptable level. However, by choosing a filler  
15 combination that maximized filler volume yet minimized  
filler surface area, both viscosity and the coefficient  
of thermal expansion were reduced. Such a combination  
was used in the reinforced syntactic foam RSF-34F shown  
in Table III, which was processable, uniform, had good  
20 physical properties, and was successfully cast in a  
metal mold.

In preparing syntactic foams by the method of the  
present invention, the hollow microspheres and graphite  
fibers, and optionally the solid microbeads, are admixed  
25 with the heat curable resin in any conventional fashion  
using a suitable mixing device such as a Waring blender.  
The homogeneous admixture is then degassed as by applying  
a vacuum. Then the mixture is loaded into a mold of  
suitable configuration from a reservoir or by using an  
30 air gun or other conventional loading device. The shape  
of the mold will, of course, determine the shape of the  
cured product and may be chosen as required to form a  
desired structure, such as an antenna waveguide. Molding  
is then accomplished in an autoclave at the temperature

1 at which the resin is curable, e.g. to 250°F to 350°F  
(121°C to 177°C), for epoxy resins generally and about  
150°F to 250°F (66 to 121°C) for the preferred epoxy  
composition described herein, at 50 to 100 psi (2586 to  
5 5171 mm Hg or 7.25 to 14.5 x 10<sup>-3</sup> Pa) for about 2 to  
about 4 hours.

Molding of the filled heat curable resin formula-  
tions to form syntactic foam composites of the present  
invention may also be effected by other conventional  
10 molding methods including transfer molding and compression  
molding procedures wherein the heat curable formulation  
is cured at the above-noted curing temperatures, using  
pressures on the order of 800 to 1000 psi (41372 to 51715  
mm Hg or 0.116 to 0.145 pascals) for 1 to 2 hours.

15 It has been found particularly advantageous to  
form the filled heat curable resin mixtures into the  
syntactic foam composites of the present invention by  
a vacuum liquid transfer molding process. In this  
procedure, the mold is first loaded with the microsphere/  
20 fiber filler which has been mechanically or manually  
premixed in predetermined proportions and pretreated  
with a sizing agent as previously described. Next,  
the mold may optionally be vibrated to promote a  
uniform distribution of the filler in the mold (e.g.  
25 about 5 minutes on a vibration table). Then the mold  
cavity is filled with the heat curable resin. The mold  
is a sealable pressure vessel constructed to support  
the vacuum/pressure sequence described below. To  
prepare for the molding process, the mold cavity is  
30 preheated to bring the cavity up to the temperature at  
which the heat curable resin is curable. A vacuum is  
then drawn on the mold to degas the mold cavity  
contents and to impregnate the filler with the resin.  
The vacuum is released to atmospheric pressure to

1 burst any gas bubbles remaining in the mold contents.  
Then, a superatmospheric pressure, such as 100 to 1000  
psi (0.01456 to 0.145 pascals), is applied to the mold  
to cause the resin to encapsulate the filler. The  
5 elevated temperature and superatmospheric pressure are  
maintained for a time sufficient to partially cure the  
resin and form a unitary structure which can be ejected  
from the mold. The ejected structure is then subjected  
to a further heating cycle to completely cure the resin.

10 By the practice of the present invention,  
reinforced syntactic foam composites are obtained  
which have a coefficient of thermal expansion of about  
25 x 10<sup>-6</sup> in/in/°F (45 x 10<sup>-6</sup> cm/cm/°C) or less  
and a density of less than 1.0 gm/cm<sup>3</sup>, as well as  
15 long-term thermal stability, amenability to being  
molded in various configurations, and ability to meet  
the NASA outgassing requirements. Using the  
preferred epoxy resin formulation described herein,  
composites are obtained which have a coefficient of  
20 thermal expansion of about 9.0 x 10<sup>-6</sup> in/in/°F (16.2  
x 10<sup>-6</sup> cm/cm/ °C) or less. In addition, the mechanical  
properties of these composites are repeatable.  
This combination of properties makes the composites of  
the present invention particularly well suited for use  
25 as a substitute for aluminum in antenna and antenna  
microwave components used in space applications. In  
particular, heat curable epoxy resins comprised of  
mixtures of tetrafunctional aromatic epoxy resins and  
liquid anhydride when heated to 150°F are sufficiently  
30 low in viscosity to accept loadings of microspheres up  
to 65 percent of the volume of the system, fiber loadings  
of up to 10 percent, and bead loadings up to 65 percent.  
These microsphere/fiber/bead filled epoxy resins are  
readily curable and when cured produce syntactic foam  
35 composites having specific gravities of between 0.8 and  
0.9 and coefficients of thermal expansion approximating

1 that of aluminum or steel. Depending on the filler  
fiber volume used in the composite of the present  
invention, composites may be tailored to have coefficients  
of thermal expansion ranging from that of the unfilled  
5 resin to that of steel.

Because of their relatively low coefficient of  
thermal expansion, epoxy resin based syntactic foam  
composites prepared in accordance with the present  
invention have been determined to be especially amenable  
10 to conventional metal plating processes, such as electro-  
less plating, when the surfaces thereof are prepared  
for plating by plasma treatment. The relatively high  
adhesion of metal deposits to the surface of the present  
composite is believed to be a function of both the  
15 topography of the plasma-treated surface plus the  
mechanical integrity of the remaining surface. The  
plasma removes the resin "skin" from the composite,  
leaving the graphite fiber/microballoon filler exposed,  
to provide a surface which is readily platable. Such  
20 metal plating of the composite of the present invention  
may be required in forming antenna components in which  
an electrically conductive surface or path is required,  
as is known in the art.

To effect plasma treatment in preparation for  
25 plating, the surface of the filler reinforced epoxy  
resin based composite is subjected to a plasma process  
with a reaction gas containing a mixture of air, nitrogen,  
or argon with oxygen, water vapor, nitrous oxide, or  
other resin oxidizing source, to remove the polymer  
30 "skin" and expose the filler, as discussed above.  
Normal plasma etching conditions known to the art are  
used. For example, for a plasma excitation energy of  
200 watts/ft<sup>2</sup> of composite, an O<sub>2</sub>/inert gas source  
of approximately 1000 ml/minute, a vacuum pressure of  
35 200 micrometers Hg, and one hour duration are used.

1           When a silver deposit is required, as in an  
antenna waveguide structure, it is advantageous to  
first form a layer of an electroless or vapor deposited  
metal such as copper to provide a conductive surface  
5       which can then be built up with additional electrolytic  
plating such as copper or silver plate to produce a  
smooth surface finish. Electrolytic silver plating may  
readily be formed on the electrolytic copper surface to  
provide a silver plated surface with good adhesion to  
10       the underlying composite material.

Electroless plating of the plasma-treated composite  
surface can be accomplished by standard procedures such  
as by dipping the plasma-treated composite in the plating  
solution for a time sufficient to achieve a continuous  
15       buildup of metal on the etched surface. Metals that  
can be plated on the molded epoxy resin based composites  
prepared in accordance with the present invention  
include, for example, copper, silver, nickel, cobalt,  
nickel/iron, nickel/cobalt, other nickel alloys, and  
20       gold. For electroless copper plating, an aqueous bath  
of Shipley Co. #328 copper plating solution may be  
used, which contains copper sulfate, sodium potassium  
tartrate, and sodium hydroxide. Other electroless  
copper plating formulations can also be employed. The  
25       plating bath is agitated or stirred prior to immersion  
of the plasma-treated composite. Preferred plating  
temperatures are in the range of about 15°C to about  
95°C (about 59°F to 203°F). Metal adhesion of this  
electroless copper plating has been determined to be  
30       excellent even after exposure of the plated composite  
to cycles of widely different temperatures, as described  
in Examples 3 and 4 herein.

1           Next, a copper plating is built up to any desired  
thickness on the electroless copper by known electrolytic  
plating methods, using commercially available electro-  
deposit copper plating solution. Finally an electrolytic  
5   silver plate is formed to the desired thickness on the  
electrolytic copper plate by known methods, using  
commercially available silver plating solution formula-  
tions. Silver plating of a composite of the present  
invention is described in Example 5.

10           The following examples illustrate but do not limit  
the present invention.

15                           EXAMPLE 1

This example illustrates a process for forming  
one type of fiber-reinforced syntactic foam composite  
in accordance with one process embodiment of the present  
invention.

20           The components of the syntactic foam formulation  
designated "S-61" are shown in Table I. The following  
details regarding the components of S-61 apply to Table I.

- a. MY720 is a tetraglycidyl methylene dianiline  
manufactured by Ciba Geigy.
- 25   b. HY906 is a nadic methyl anhydride hardener  
manufactured by Ciba Geigy.
- c. BDMA is benzyldimethylamine accelerator  
available from E.V. Roberts or Ciba Geigy.
- d. D32/4500 microspheres are borosilicate  
30   microspheres having a mean diameter of 75  
micrometers, a specific gravity of 0.32, and a  
compressive strength of 4500 psi, available from  
the 3M Company.

- 1 e. GY70 fibers are graphite fibers milled to a  
length of about 150 micrometers and having a  
diameter of about 8 micrometers, available from  
the Celanese Corporation.
- 5 f. KR38S, KR55, and KR9S are titanate coupling  
and wetting agents, available from Kenrich  
Petrochemical Company, Bayonne, New Jersey.
- g. AF4 is a surfactant, available from Furane  
Chemical Co.

TABLE I

## COMPOSITION OF FORMULATION S61

| Component                             | PHR* | Weight (grams) |
|---------------------------------------|------|----------------|
| 1. Resin                              |      |                |
| MY720 epoxy resin                     | 100  | 400            |
| HY906 hardener                        | 100  | 1.0            |
| BDMA accelerator                      | 0.25 | 4.0            |
| KR38S                                 | 1.0  | 4.0            |
| 2. Microspheres                       |      |                |
| D32/4500                              | 40   | 160            |
| KR55                                  | 0.3  | 1.2            |
| AF4 (Optional)                        | 0.2  | 0.8            |
| 3. Fibers                             |      |                |
| Milled GY70                           | 20   | 80             |
| KR9S                                  | 0.2  | 0.8            |
| *PHR is parts per hundred epoxy resin |      |                |



### Preparation of Graphite Fibers

1           The GY70 graphite fibers in continuous tow form  
were cut into lengths of approximately 1/8 inch to 1/2  
inch (0.32 to 1.27 centimeters), using a paper cutter.  
5       Batches of the chopped fibers (approximately 80 grams  
each) were loaded into a ball mill jar having a one-  
gallon capacity and sufficient Freon TF was added to  
cover the ceramic balls to serve as a suspension medium.  
The fibers were milled for 24 hours. Scanning electron  
10       micrographs of the milled fibers showed them to be  
broken into small fragments ranging from approximately  
2 to 10 micrometers in length.

          The milled fibers and Freon were poured into a  
shallow stainless steel pan, and the Freon was allowed  
15       to evaporate. The fibers were then dried 4 hours in an  
air-circulating oven set at 250°F (121°C) and sifted  
on a vibration plate to pass a 325 mesh screen. The  
dried, sifted fibers were stored in a desiccator box  
until ready for use.

### Composite Formation

20           The formulation S61 was prepared as follows. A  
one-gallon hot/cold pot for a Waring blender was heated  
to 140°F (60°C) using a temperature-controlled water  
25       bath. The premeasured amount of the HY906 hardener was  
put in the blender and the mixer speed was adjusted  
using a Variac variable potentiometer so that the  
hardener was just barely agitated. With the blender on  
"low" setting, the Variac was turned to 70 percent of  
30       full speed. The resin, which had been preheated to  
160°F (71°C), was added to the pot and the contents of  
the pot were mixed until the mixture appeared homogeneous  
(about 5 minutes), and then cooled to room temperature.

1 Next, there was gradually added to the pot the KR38S,  
AF4 (optional), and 25 percent of the milled fibers  
which had been previously dried overnight in an oven at  
200°F (93°C) and fluffed by running in the blender on  
5 "low" speed at 70 percent of the full Variac speed for  
about 15 seconds for 5 grams of fiber. The mixture was  
mixed for about 5 minutes. Next, 10 percent of the  
microspheres which had been dried overnight in an oven  
at 200°F (93°C) was gradually added and the contents of  
10 the pot were mixed until streaks of microspheres disap-  
peared. The remaining amount of fiber and the KR9S  
were gradually added and the pot contents mixed for  
about 30 minutes. Next, the BDMA was added slowly,  
followed by the KR55 and the remaining amount of micro-  
15 spheres. The pot contents were mixed until streaks of  
microspheres disappeared.

Then, the pot was covered and a vacuum pump was  
attached to the pot with the pump set to pull a vacuum  
of 22 inches (559 mm) of mercury. The mixer was run  
20 for 45 minutes under vacuum or until there were no  
black streaks of fibers in the mixture. Finally, the  
mixture was carefully poured so as to minimize air  
entrapment, into a preheated stainless steel test  
specimen mold which had been prepared by: cleaning  
25 with methyl ethyl ketone solvent, baking at 300°F (149°C)  
for 30 minutes, brushing with a fluorocarbon mold  
release agent to provide three coats of the release  
agent with 30 minutes air drying for each coat, and  
preheating to 140°F (60°C). (Optionally, the formulation  
30 was injected with an air gun into the mold.) After  
pouring the mixture into the mold, the mold was vibrated  
on a vibrating table for 5 minutes at the maximum safe  
speed, with a large, flat, 0.5 inch thick aluminum  
plate placed on top of the mold. Next, the mold was

1 placed in an oven preheated to 275°F (135°C) and a  
thermocouple was placed on/in each of the following: on  
the mold, in the oven, and in the mold contents through  
a hole in the side wall of the mold. When the thermo-  
5 couple in the mold contents registered 275°F (135°C),  
the following cure cycle was run: 10 minutes at 275°F  
(135°C); 10 minutes at 300°F (149°C); 120 minutes at  
350°F (177°C). The maximum oven rate was used for  
changing temperatures.

10 The mold was removed from the oven and was  
disassembled, and the part was removed from the mold  
while the mold was still hot, being sure to keep the  
thermocouple embedded in the syntactic foam. The part  
was deflashed as necessary with a file. For the post-  
15 cure, the demolded part was placed in an oven preheated  
to 400°F (204°C) between 0.5 inch thick aluminum plates,  
with 2-5 kilograms weight on the top plate. When the  
thermocouple in the syntactic foam registered 400°F  
(204°C), the following post-cure cycle was run: 1 hour  
20 at 400°F (204°C); 1 hour at 425°F (218°C); 1 hour at  
450°F (232°C), and 1 hour at 475°F (246°C) Finally, the  
part was removed from the oven.

The fiber reinforced syntactic foam composite  
formed as described above was found to have the properties  
shown in Table II. With regard to Table II, the  
25 following test requirements apply:

- a. CTE was determined using a quartz  
dilatometer to measure the change in  
length as a function of temperature.
- 30 b. Specific gravity was measured using a  
pycnometer.
- c. Viscosity was measured with a Brookfield  
Viscometer.

- 1 d. Shrinkage was measured by determining the  
dimensional difference between the molded  
product and the mold.
- 5 e. Gel time was determined qualitatively as  
the time required for the liquid resin to  
form a gel.
- 10 f. Pot life was determined qualitatively as  
the time required for the liquid resin  
to increase in viscosity to the point of  
being unworkable.
- 15 g. Degree of exotherm was determined by  
using a differential scanning calorimeter.

TABLE II  
PROPERTIES OF COMPOSITE OF S61 FORMULATION

| Property                    | Value  |
|-----------------------------|--|
| CTE                         | 19-22 x 10 <sup>-6</sup> cm/cm/°C<br>10.6-12.7 x 10 <sup>-6</sup> in/in/°F |
| Specific gravity            | 0.80   |
| Viscosity at 150°F (65.6°C) | 35,000 centipoise  |
| Shrinkage                   | 0.8%   |
| Gel time                    | >60 minutes  |
| Pot life                    | >360 minutes   |
| Degree of exotherm          | 15°F (8.3°C)   |

EXAMPLE 2

This example illustrates a process for forming fiber-reinforced syntactic foam composites of various compositions in accordance with the present invention.

The components of the various formulations designated as the "RSF series" are shown in Table III. The following details regarding the specific components apply to Table III.

- a. Epoxy is a mixture of 70 parts Glyamine 135 (diglycidyl ortho toluidine) and 30 parts Glyamine 120 (tetraglycidyl methylene dianiline), both materials obtained from FIC Resins of San Francisco, California, mixed with about 115 parts nadic methyl anhydride hardener and about 0.25 parts benzyldimethylaniline accelerator.
- b. Zeeospheres 0/8 are solid glass spheres having a median diameter of 3 micrometers, available from Zeelan Industries of St. Paul, Minnesota.
- c. Carbospheres Type A are hollow carbon spheres having an average diameter of 50 micrometers, available from Versar of Springfield, Virginia.
- d. 3M A 32/2500 glass bubbles are glass microspheres having a mean diameter of 50 micrometers, a specific gravity of 0.32, and a compressive strength of 2500 psi, available from the 3M Company of Minnesota.
- e. 3M A 16/500 are glass microspheres having a mean diameter of 75 micrometers, a specific gravity of 0.16, and a compressive strength of 500 psi, available from the 3M Company.
- f. Eccospheres SI are hollow silica microspheres having a diameter of 45-125 micrometers, available from Emerson and Cuming Inc. of Canton, Massachusetts.

- 1           g. Grefco 213 R40 beads are solid glass micro-  
            spheres having a diameter of 3-8 micrometers,  
            available from Grefco Inc. of Torrance,  
            California.
- 5           h. HM-S 50 (50 $\mu$ ) are graphite fibers having a  
            length of about 50 micrometers and a diameter  
            of about 8 micrometers, available from  
            Courtaulds Co. of the United Kingdom.
- 10          i. AS 50 (250 $\mu$ ) graphite are graphite fibers  
            having a length of about 250 micrometers and  
            a diameter of about 8 micrometers, available  
            from Courtaulds of the United Kingdom.
- 15          j. 0.063" HMS-50 (1/16") are graphite fibers  
            having a length of about 1600 micrometers  
            and a diameter of about 8 micrometers,  
            available Finn and Fram of Sun Valley,  
            California.

20          Using each of the formulations of the RSF series  
            designated in Table III, a fiber-reinforced syntactic  
            foam composite was formed following the general procedure  
            set forth in Example 1. The properties of each of  
            these composites is shown in Table IV. The following  
25          test requirements were applied for the measurements in  
            Table IV.

30

35

- a. Density was determined by pycnometer.
- b. CTE was determined using a quartz dilatometer to measure the change in length ( $\Delta l$ ) as a function of temperature.
- c. Compressive strength was determined using the American Society for Testing and Materials (ASTM) Standard No. D695.
- d. Compressive modulus was determined using ASTM D695, using crosshead speed in place of strain gauges.
- e. Uniformity was determined by visual inspection.
- f. Viscosity was measured with a Brookfield Viscometer.

TABLE III

## COMPOSITION OF FORMULATIONS OF RSF SERIES

| RSF-<br>FORMULATION | EPOXY | VOLUME RATIO OF FOAM FILLERS |                        |                              |                   |                             |                           |                          |
|---------------------|-------|------------------------------|------------------------|------------------------------|-------------------|-----------------------------|---------------------------|--------------------------|
|                     |       | MICROSPHERES                 |                        |                              |                   |                             | FIBERS                    |                          |
|                     |       | ZEOSPHERES<br>0/8            | CARBOSPHERES<br>TYPE A | 3M A32/2500<br>GLASS BUBBLES | ECCOSPHERES<br>SI | GREFCO<br>213 R 40<br>BEADS | HM-S 50 $\mu$<br>GRAPHITE | 0.063" HMS-50<br>(1/16") |
| 3                   | 0.405 | 0.098                        |                        | 0.471                        |                   |                             | 0.025                     |                          |
| 4                   | 0.375 | 0.048                        |                        | 0.514                        |                   |                             | 0.064                     |                          |
| 5                   | 0.401 |                              |                        | 0.500                        |                   | 0.059                       | 0.040                     |                          |
| 6                   | 0.401 |                              |                        | 0.500                        |                   | 0.059                       | 0.034*                    |                          |
| 7                   | 0.536 | 0.057                        |                        | 0.400                        |                   |                             |                           | 0.007                    |
| 8                   | 0.530 | 0.057                        |                        | 0.395                        |                   |                             |                           | 0.018                    |
| 13                  | 0.536 | 0.057                        |                        | 0.400                        |                   |                             | 0.007                     |                          |
| 14                  | 0.530 | 0.057                        |                        | 0.395                        |                   |                             | 0.018                     |                          |
| 19                  | 0.37  | 0.05                         |                        | 0.51                         |                   |                             | 0.06                      |                          |
| 20                  | 0.322 | 0.041                        |                        |                              | 0.586             |                             | 0.050                     |                          |
| 21                  | 0.375 | 0.048                        |                        | 0.514                        |                   |                             | 0.064                     |                          |
| 23                  | 0.583 | 0.023                        | 0.368                  |                              |                   |                             | 0.026                     |                          |
| 25                  | 0.503 | 0.022                        | 0.450                  |                              |                   |                             | 0.025                     |                          |
| 26                  | 0.583 | 0.023                        | 0.368                  |                              |                   |                             | 0.026                     |                          |
| 28                  | 0.583 | 0.023                        | 0.368                  |                              |                   |                             | 0.026                     |                          |
| 29                  | 0.583 | 0.023                        | 0.368                  |                              |                   |                             | 0.026                     |                          |
| 31                  | 0.496 | 0.022                        |                        | 0.457                        |                   |                             | 0.025                     |                          |
| 33                  | 0.503 | 0.022                        |                        |                              | 0.450             |                             | 0.025                     |                          |
| 34                  | 0.394 | 0.026                        |                        | 0.550                        |                   |                             | 0.030                     |                          |
| 34F                 | 0.410 | 0.025                        |                        | 0.530                        |                   |                             | 0.035                     |                          |
| 35                  | 0.353 | 0.028                        |                        | 0.588**                      |                   |                             | 0.032                     |                          |
| 36                  | 0.383 | 0.026                        |                        |                              | 0.560             |                             | 0.031                     |                          |

\* Plus 0.007 of AS 50 (250 ) graphite  
 \*\* 3M A16/500 used in place of A32/2500



| RSF-FORMULATION | DENSITY (g/cc) | CTE (10 <sup>-6</sup> in/in/°F) | COMPRESSIVE STRENGTH (psi)* | COMPRESSIVE MODULUS (10 <sup>3</sup> psi)* | UNIFORMITY (1-10) | VISCOSITY |
|-----------------|----------------|---------------------------------|-----------------------------|--|-------------------|-----------|
| 3               | 0.898          | 16.82                           | 15,300                      | 394  | 3.7               | 5         |
| 4               | 0.881          | 13.81                           | 16,300                      | 447  | 4.3               | 4         |
| 5               | 0.872          | 15.10                           | 16,400                      | 406  | 4.0               | 4         |
| 6               | 0.869          | 22.16                           | 14,300                      | 407  | 3.5               | 5         |
| 7               | 0.968          | 20.82                           | 15,100                      | 394  | 2.7               | 8         |
| 8               | 0.982          | 21.39                           | 18,400                      | 410  | 4.7               | 7         |
| 13              | 1.000          | 25.46                           | 14,900                      | 386  | 2.3               | 7         |
| 14              | 1.019          | 25.55                           | 15,400                      | 405  | 1.8               | 6         |
| 19              | 0.852          | 14.06                           | 13,200                      | 411  | 4.0               | 3         |
| 20              | 0.694          | 14.09                           | 8,600                       | 335  | 2.7               | 2         |
| 21              | 0.8561         | 17.02                           | 14,000                      | 439  | 3.4               | 3         |
| 23              | 0.9912         | 20.69                           | 16,300                      | 384  | 5.5               | 7         |
| 25              | 1.0387         | 30.51                           | 19,000                      | 423  | --                | 6         |
| 26              | 1.005          | 21.73                           | 15,700                      | 395  | 7.3               | 5         |
| 28              | 0.982          | 20.10                           | 17,100                      | 411  | 6.5               | 5         |
| 29              | 1.002          | 20.70                           | 17,800                      | 393  | 7.6               | 5         |
| 31              | 0.888          | 23.90                           | 17,800                      | 400  | 6.6               | 8         |
| 33              | 0.815          | 23.10                           | 13,300                      | 343  | 3.9               | 7         |
| 34              | 0.824          | 14.59                           | 17,500                      | 394  | 4.4               | 6         |
| 34F             | 0.842          | 14.24                           | 17,300                      | 425  | --                | --        |
| 35              | 0.738          | 17.23                           | 10,200                      | 303  | 4.0               | 6         |
| 36              | 0.745          | 17.14                           | 12,100                      | 335  | 3.0               | 5         |

\* 1 psi = 1.45 x 10<sup>-4</sup> pascals

\* 1 psi =  $1.45 \times 10^{-4}$  pascals

EXAMPLE 3

This example illustrates the formation of a fiber-reinforced syntactic foam composite using the preferred epoxy resin formulation and preferred vacuum liquid transfer molding process described herein.

The heat curable epoxy resin formulation had the following composition:

| <u>Resin Component</u>     | <u>WT. (gms.)</u> |
|----------------------------|-------------------|
| Diglycidyl orthotoluidine  | 100               |
| Nadic methylanhydride      | 100               |
| 2-ethyl-4-methyl imidazole | 2                 |

This composition had a gel time of 25 minutes, a viscosity of 220 centipoise at 75°F (24°C), and a CTE of 30.8 to 32.3 x 10<sup>-6</sup> in/in/°F (55.8 to 58.1 x 10<sup>-6</sup> cm/cm/°C).

A filler mixture was prepared having the composition shown below and a density of 0.543 gm/cm<sup>3</sup>. Carbospheres are hollow carbon microballoons having a mean diameter of about 50 micrometers, available from Versar Inc. of Springfield, Virginia. HM-S graphite fibers are graphite fibers having a length of about 50 micrometers, available from Courtaulds Co. of the United Kingdom. Titanate sizing agents are available from Kenrich Petrochemical Co. of Bayonne, New Jersey.

| 1 | <u>Filler Component</u>         | <u>WT. (gms.)</u> |
|---|---------------------------------|-------------------|
|   | Carbosphere, 50 micrometers     | 50                |
|   | HM-S fiber, 50 micrometers      | 50                |
| 5 | Titanate sizing agent<br>KR238M | 1                 |

10 Using the above-noted resin and filler, each of a series of resin/filler formulations shown in Table V was processed as described below in order to form the composite of the present invention.

15 The filler composition (i.e. a mixture of the fibers and microspheres pretreated with the sizing agent as previously described herein) was loaded into a cleaned 5.5 inch x 0.5 inch (14cm x 1.3cm) wide slab mold internally coated with a polyvinyl alcohol release agent. The mold was preheated to 212°F (100°C), the temperature at which hardening of the heat curable epoxy resin formulation was initiated. The epoxy resin formulation was poured into the mold containing the filler. The mold was placed in a laminating press, a nylon vacuum bag was constructed around the compression tooling of the press, and a vacuum pressure of 125 millimeters (mm) mercury pressure (166,625 pascals) was maintained on the assembly for 2 minutes to draw down the resin to impregnate the filler and to degas the resin materials in the mold. The vacuum was then released without removal of the vacuum bag and the assembly held in this passive vacuum state for an additional 2 minutes. Thereafter, a constant positive pressure of approximately 800 pounds per square inch (41,360 mm Hg or  $5.5 \times 10^6$  pascals) was imposed on the resin/filler mixture in the mold for 2 hours at 212°F (100°C). During this pressurization stage, the resin was bled from the mold in the amount noted in Table V.

1 The molded composite slab had sufficient green strength  
to be ejected from the mold, whereafter it was post  
cured for 4 hours unrestrained, in an oven set at 300°F  
(149°C). The final void-free slab contained the filler  
5 ratio noted in Table V and was cut into appropriate  
shapes for physical testing. The composite was found  
to have the physical properties which are summarized in  
Table VI. As indicated by the values for CTE given in  
Table VI, unexpected significant improvement in the CTE  
10 of these composites was obtained using the preferred  
resin composition and filler compositions described  
herein.

In addition, a typical sample was tested in  
accordance with ASTM E-595-77 and found to have a  
15 collected volatile condensible material (CVCM) of less  
than 0.1 percent and a total mass loss (TML) of less  
than 1 percent, which meets the NASA outgassing  
requirements.

Further, for Specimen 1 of Table V, a portion  
20 of the molded slab was surface plated with copper by  
subjecting the surface of the slab to an oxygen rich  
plasma treatment, as previously described. The treated  
slab was then dipped into Shipley #328, electroless  
copper plating solution, as previously described, and  
25 then dried at 248°F (120°C) under 29 inches (737mm) Hg  
(guage pressure).

The plated composite was then evaluated for  
adhesion of the deposited copper layer using an ASTM  
D3359 tape adhesion test before and after 25 cycles of  
30 thermal shock imposed on the plated surface by alternately  
dipping the plated specimen in liquid nitrogen (-320°F  
or -196°C) for 30 seconds and boiling water (212°F or  
100°C) for 10 seconds. No loss of copper was observed.

TABLE V  
COMPONENTS OF MOLDING COMPOSITION

| Specimen No. | Resin (gms.) | Filler (gms.) | Filler Ratio |         | Resin Bleed During Molding % |
|--------------|--------------|---------------|--------------|---------|------------------------------|
|              |              |               | (Wt.%)       | (Vol.%) |                              |
| 1            | 40           | 10            | 45           | 64      | 69.2                         |
| 2            | 30           | 9.4           | 38           | 57      | 47.8                         |
| 3            | 30           | 9.4           | 38           | 57      | 47.9                         |
| 4            | 17.0*        | 5.5           | 37           | 57      | 45.3                         |
| 5            | 19.0*        | 6.0           | 39           | 59      | 50.6                         |
| 6            | 20.7*        | 6.5           | 41           | 60      | 54.6                         |

\* KR134S sizing agent was substituted for the previously noted sizing agent.

$$** \text{ Resin bleed} = \left( \frac{W_1 - W_2}{W_1} \right) 100$$

where  $W_1$  = initial resin weight

$W_2$  = resin displaced from the mold, using a bleeder cloth.

Vol. % calculated from resin bleed varies about 10-20% of the actual vol. % value.

TABLE VI  
PHYSICAL PROPERTIES OF MOLDED COMPOSITES

| Specimen<br>No.                          | Thickness<br>(in.) | Density<br>gm/cm <sup>3</sup> | CTE*<br>10 <sup>-6</sup> cm/cm/°C<br>(10 <sup>-6</sup> in/in/°F) |
|--|--------------------|-------------------------------|--|
| 1  | 0.478              | 0.743                         | 6.6 (3.6)  |
| 2  | 0.550              | 0.900                         | 16.2 (9.0)   |
| 3  | 0.565              | 0.876                         | 14.2 (8.1)   |
| 4  | 1.070              | 0.889                         | --   |
| 5  | 1.042              | 0.915                         | --   |
| 6  | 1.065              | 0.914                         | --   |
| * Determined using a quartz dilatometer. |                    |                               |  |

EXAMPLE 4

1 This example illustrates the formation of composites  
as set forth in Example 3 with the exception that the  
composition of the filler formulation was varied. The  
5 procedure set forth in Example 3 was followed except  
that the filler compositions shown in Table VII were  
used. The following details regarding the specific  
components apply to Table VII.

- 10 a. Carbospheres are carbon microspheres having  
a specific gravity of 0.32 and a mean diameter  
of 50 micrometers, available from Versar  
Corporation.
- b. HM-S 50 (50 $\mu$ ) graphite fibers are graphite  
15 fibers having a length of about 50 micrometers  
and a diameter of about 8 micrometers, available  
from the Courtaulds Co. of the United Kingdom.
- c. 1/4 mm HM-S 50 graphite fibers are graphite  
fibers having a length of about 250 micrometers  
and a diameter of about 8 micrometers,  
20 available from the Courtaulds Co. of the  
United Kingdom.
- d. C15/250 glass microballoons are composed of  
borosilicate glass, have a diameter of 10-200  
micrometers, a density of 0.15 gm/cm<sup>3</sup>, and  
25 a compressive strength of 250 psi, available  
from the 3M Company of Minnesota.

The physical properties of the molded composite  
30 slabs so formed are set forth in Table VIII.

TABLE VII  
COMPOSITION OF FILLER FORMULATIONS

| Filler<br>No. | Density<br>(gm/cm <sup>3</sup> ) | Carbosphere<br>Microballoons<br>(gms) | HM-S 50 (50 $\mu$ )<br>graphite<br>fiber (gms) | 1/4mm HM-S 50<br>graphite<br>fiber (gms) | Cl5/250<br>glass<br>micro-<br>balloons<br>(gms) | Titanate<br>Sizing Agent |               |
|---------------|----------------------------------|---------------------------------------|--|--|---|--------------------------|---------------|
|               |                                  |                                       |  |  |   | KR238M<br>(gms)          | KR55<br>(gms) |
| A             | 0.543                            | 50                                    | 50   | --                                       | --  | 1                        | --            |
| B             | 0.328                            | 20                                    | 15   | --                                       | 10  | --                       | 0.5           |
| C             | 0.387                            | --                                    | 4.4  | 45.6                                     | 25  | 1                        | --            |



TABLE VIII

## PHYSICAL PROPERTIES OF MOLDED COMPOSITE SLABS

| Filler<br>Used in<br>Molded<br>Sample | Thickness<br>(in.) | Density<br>(gm/cm <sup>3</sup> ) | Filler Ratio |         | Resin<br>Bleed<br>% | Cu<br>Coating<br>Removed |
|---------------------------------------|--------------------|----------------------------------|--------------|---------|---------------------|--------------------------|
|                                       |                    |                                  | (Wt.%)       | (Vol.%) |                     |                          |
| A                                     | 0.443              | 1.050                            | 39           | 59      | 51.0                | ≤ 5%                     |
| B                                     | 0.540              | 0.753                            | 26-47        | 56-77   | 61.9                | ≤ 5%                     |
| C                                     | 0.850              | 0.948                            | 27           | 54      | 16.2                | 5-15%                    |

In addition, the surfaces of the molded composite slabs of Table VIII were then subjected to plasma treatment under the following conditions: O<sub>2</sub>/inert gas source of approximately 1000 ml/minute, vacuum pressure of 200 $\mu$  Hg, and one hour duration. The surfaces of the plasma etched slabs were then copper plated to a thickness of about 3-4 mils by dipping the etched slabs in an aqueous Shipley #328 electroless copper plating bath.

The plated composite was then evaluated for adhesion of the deposited copper layer using the ASTM D3359 tape adhesion test and thermal shock cycle of Example 3. The adhesion results are recorded in Table VIII, indicating the amount of copper coating on lattice removed by the tape.

EXAMPLE 5

1 A syntactic foam composite prepared from Specimen  
No. 2 of Table V described in Example 3 and molded in  
a slab mold was plated with silver as follows. The  
5 surface of the slab was subjected to an oxygen rich  
plasma etch which resulted in the removal of the surface  
polymer "skin," as previously described. The etched  
slab was then metallized using the Shipley Company  
#328 electroless copper plating solution process, as  
10 previously described, and thoroughly rinsed and dried  
at 248°F (120°C) under 29 inches (725 mm) Hg (gauge  
pressure), to provide a layer of electroless copper  
20 microinches ( $5.08 \times 10^{-5}$  cm) thick. Next, the  
slab was immersed in an acid copper electrolytic plating  
15 bath at 25°C for 25 minutes to form an electrodeposited  
copper layer 100 microinches ( $2.54 \times 10^{-4}$  cm) thick.  
Finally, the copper-plated slab was immersed in an  
electrolytic silver plating bath at 25°C for 25 minutes  
to form a layer of silver 300 microinches ( $7.62 \times 10^{-4}$  cm)  
20 thick.

The silver-plated slab was then evaluated for  
adhesion of the deposited layer using an ASTM D3359  
tape adhesion test before and after 25 cycles of thermal  
shock imposed on the plated surface by alternately  
25 dipping the plated specimen in liquid nitrogen (-328°F  
or -196°C) for one minute and boiling water (212°F or  
100°C) for one minute. No adhesion loss of silver was  
observed.

The silver-plated syntactic foam had the same low  
30 R.F. loss characteristics as aluminum when tested for  
insertion loss at 4.6 gigahertz using standard electronic  
tests. Thus, with the use of proper tooling for molding,  
antenna waveguide structures may be formed from the  
composite of the present invention, which are effective  
35 microwave or antenna components and which meet the

1 requirements for use in space applications. Syntactic  
foams plated with metals such as silver and copper may  
serve as metal-plated core materials for both microwave  
components and microwave reflectors.

5 The fiber-reinforced syntactic foam composites of  
the present invention achieve a 3-to-1 reduction in  
weight in comparison with aluminum, which makes these  
components attractive for weight-sensitive applications  
in a spacecraft environment. At the same time, however,  
10 in situations calling for high volume production, the  
readily-moldable nature of the reinforced foam mixture  
disclosed herein further offers the potential of signi-  
ficantly reduced cost in comparison with the machining  
traditionally employed for the production of conventional  
15 metal parts.

The preceding description has presented in detail  
exemplary preferred ways in which the concepts of the  
present invention may be applied. Those skilled in the  
art will recognize that numerous alternatives encompassing  
20 many variations may readily be employed without departing  
from the intention and scope of the invention set forth  
in the appended claims. In particular, the present  
invention is not limited to the specific resin, fibers,  
or microballoons set forth herein as examples. By  
25 following the teachings provided herein relating to the  
effect of each component of the mixture on the final  
composite and the effect of the various components on  
each other, other suitable resin, fiber, and microballoon  
materials may readily be determined. Further, by  
30 following the teachings provided herein, it may be  
determined how to form composite materials having a  
density or coefficient of thermal expansion other than  
those set forth herein as required for the specifically  
mentioned end use in space applications.

35

MEL:tp

[170-2]

CLAIMSWhat is Claimed is:

- 1           1. A fiber-reinforced syntactic foam composite  
having a specific gravity less than 1.0 and a coefficient  
of thermal expansion of about  $25 \times 10^{-6}$  in/in/°F  
( $45 \times 10^{-6}$  cm/cm/°C) or less, the composite being  
5           prepared from an admixture comprising a heat curable  
thermosetting resin, hollow microspheres having a  
diameter in the range of about 5 to about 200 micrometers  
and fibers having a length less than or equal to 250  
micrometers.
- 1           2. The composite of Claim 1 wherein the resin  
comprises a material selected from the group consisting  
of an epoxy, a polyester and a condensate of formaldehyde.
- 1           3. The composite of Claim 2 wherein the heat  
curable thermosetting resin comprises a mixture of an  
epoxy resin and a polyfunctional curing agent.
- 1           4. The composite of Claim 3 wherein the epoxy  
resin is tetraglycidyl methylene dianiline, a mixture  
of diglycidyl orthotoluidine and tetraglycidyl methylene  
dianiline, the diglycidyl ether of Bisphenol A, or  
5           a phenol formaldehyde novolac polyglycidyl ether.

1           5. The composite of Claim 3 wherein the polyfunctional curing agent is a polyamine, a polycarboxylic acid anhydride, or the maleic anhydride adduct of methyl cyclopentadiene.

1           6. The composite of Claim 3 wherein the mixture further comprises benzyldimethylaniline as an accelerator.

1           7. The composite of Claim 1 wherein the hollow microspheres are formed of glass, silica, carbon, acrylate resins, or phenolic resins.

1           8. The composite of Claim 7 wherein the hollow microspheres are formed of glass and have an average diameter of about 50 micrometers.

1           9. The composite of Claim 7 wherein the hollow microspheres comprise a mixture of glass microspheres and carbon microspheres.

1           10. The composite of Claim 1 wherein the fibers are formed of graphite, glass, carbon, nylon, or polyamide.

1           11. The composite of Claim 10 wherein the fibers are formed of graphite and have a length of about 50 micrometers and a diameter of about 8 micrometers.

1           12. The composite of Claim 1 wherein said admixture  
further includes a coupling and wetting agent.

1           13. The composite of Claim 1 wherein the admixture  
further includes solid microbeads.

1           14. The composite of Claim 1 which comprises  
about 35 to about 65 percent by volume microspheres  
and about 3 to about 10 percent by volume fibers, the  
balance being a matrix comprised of the heat cured  
5 resin throughout which the microspheres and fibers are  
dispersed and bonded together.

1           15. The composite of Claim 14 which additionally  
comprises about 2 to about 8 percent by volume of solid  
microbeads having a diameter of about 2 to about 8  
micrometers.

1           16. A fiber-reinforced syntactic foam composite  
as set forth in Claim 1, wherein said heat curable  
thermosetting resin comprises an uncured polyglycidyl  
aromatic amine, a polycarboxylic acid anhydride curing  
5 agent, and a curing accelerator selected from the  
group consisting of substituted imidazole compounds  
and organometallic compounds, and said composite has a  
specific gravity less than 1.0 and a coefficient of  
thermal expansion of about  $9.0 \times 10^{-6}$  in/in/°F  
10 ( $16.2 \times 10^{-6}$  cm/cm/°C) or less.

1           17. The composite of Claim 16 wherein the  
polyglycidyl aromatic amine is diglycidylaniline,  
diglycidyl orthotoluidine, or tetraglycidyl  
metaxylylene diamine.

1           18. The composite of Claim 16 wherein the  
polycarboxylic acid anhydride is present in sufficient  
quantity to react with from about 60 to about 90 percent  
of the epoxide groups in said polyglycidyl aromatic  
5 amine.

1           19. The composite of Claim 16 wherein the  
polycarboxylic acid anhydride is nadic methyl anhydride,  
methyl tetrahydrophthalic anhydride, or methyl  
hexahydrophthalic anhydride.

1           20. The composite of Claim 16 wherein said curing  
accelerator is present in the amount of about 0 to  
about 3 percent, by weight.

1           21. The composite of Claim 16 wherein said curing  
accelerator is 2-ethyl-4-methyl imidazole or stannous  
octoate.

1           22. The composite of Claim 16 wherein:

a) said uncured polyglycidyl aromatic amine  
is diglycidyl orthotoluidine and is present in the  
amount of about 100 parts per hundred resin by weight;

5           b) said curing agent is nadic methyl anhydride  
and is present in the amount of about 100 parts per  
hundred resin by weight; and

10           c) said curing accelerator is 2-ethyl-4-  
methyl imidazole and is present in the amount of about  
2 parts per hundred resin by weight.

1           23. A fiber-reinforced syntactic foam composite  
as set forth in Claim 16, comprising:

a) a heat curable thermosetting epoxy resin  
comprising:

- 5           1) diglycidyl orthotoluidine in the  
amount of about 100 parts per hundred  
resin by weight;  
2) nadic methyl anhydride in the amount  
of about 100 parts per hundred resin  
10 by weight; and  
3) 2-ethyl-4-methyl imidazole in the  
amount of about 2 parts per hundred  
resin by weight;

b) hollow carbon microspheres having a  
15 diameter in the range of about 20 to about 200  
micrometers; and

c) graphite fibers having a length of less  
than or equal to 250 micrometers and a diameter of  
about 8 micrometers.

1           24. The composite of Claim 1 wherein:

a) the heat curable thermosetting resin  
comprises a mixture of diglycidyl orthotoluidene,  
tetraglycidyl methylene dianiline, nadic methyl anhydride,  
5 and benzyldimethylaniline;

b) the hollow microspheres are glass  
microspheres having a mean diameter of 50 micrometers;

c) the fibers are graphite fibers having a  
length of about 50 micrometers and a diameter of about  
10 8 micrometers; and

d) the admixture further comprises solid  
glass microbeads having a median diameter of 3  
micrometers.



1           25. A fiber-reinforced syntactic foam composite  
as set forth in Claim 1, comprising:

5           a) a heat curable thermosetting epoxy  
resin comprising a mixture of tetraglycidyl methylene  
dianiline, nadic methyl anhydride, and benzyldimethyl-  
aniline;

          b) hollow glass microspheres having a mean  
diameter of about 75 micrometers; and

10           c) graphite fibers having a length of about  
150 micrometers and a diameter of about 8 micrometers.

1           26. An article of manufacture comprising a body  
formed from the composite material of Claim 1.

1           27. The article of manufacture set forth in Claim  
26 which further comprises a layer of electrically  
conductive material adhered to selected surfaces of the  
body.

1           28. The article of manufacture set forth in Claim  
27 wherein said article comprises a component in an  
antenna structure.

1           29. A method for fabricating a fiber-reinforced  
syntactic foam composite as set forth in Claims 1-25,  
which comprises the steps of:

5           a) admixing a heat curable thermosetting  
resin, hollow microspheres having a diameter in the  
range of about 5 to about 200 micrometers and fibers  
having a length less than or equal to 250 micrometers  
to form a mixture of the resin, microspheres and fibers;  
and

10                   b) curing the mixture of the resin,  
microspheres, and fibers in a mold of predetermined  
geometry to a thermoset state to provide a composite  
structure containing about 35 to about 65 volume percent  
15                   microspheres and about 3 to about 10 volume percent  
fibers dispersed throughout the resin matrix, and the  
resin comprising the balance of the composite, wherein  
the composite has a specific gravity of less than 1.0  
and a coefficient of thermal expansion of about  
13 x 10<sup>-6</sup> in/in/°F (23 x 10<sup>-6</sup> cm/cm/°C) or less.

1                   30. The method of Claim 29 wherein the admixing  
comprises:

- 5                   a) forming a liquid dispersion of the  
microspheres and fibers in a coupling agent;
- b) filtering the dispersion to separate the  
microspheres and fibers from the liquid as a filtration  
residue;
- c) drying the residue to provide a mixture  
of microspheres and fibers coated with the coupling  
10                  agent; and
- d) admixing the coated microspheres and  
fibers with the resin.

1                   31. The method of Claim 30 wherein:

- a) the microspheres are hollow glass  
microspheres;
- b) the fibers are graphite fibers;
- 5                   c) the coupling agent is selected from the  
group consisting of a silane compound and a titanate  
compound.

# INTERNATIONAL SEARCH REPORT

International Application No **PCT/US 85/00625**

| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup><br>According to International Patent Classification (IPC) or to both National Classification and IPC<br><b>IPC<sup>4</sup>: C 08 J 9/32; C 08 L 63/00; H 01 Q 15/14; C 08 K 7/00</b>  |  |                                     |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
|---|--|-------------------------------------|---|--|--|--|--|----------------------------|---|----|--|---|--|----------------------------|---|----|--|---|---|------------------------------|---|----|--|---|--|---|---|----|--|---|--|------------|---|----|--|---|---|--|
| <b>II. FIELDS SEARCHED</b><br><div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched <sup>7</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 25%; border-bottom: 1px solid black;">Classification System</th> <th style="width: 75%; border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="vertical-align: top; padding: 5px;">IPC<sup>4</sup></td> <td style="vertical-align: top; padding: 5px;">C 08 J; C 08 K<br/>C 08 L;<br/>H 01 Q;</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation<br/>to the Extent that such Documents are Included in the Fields Searched <sup>8</sup></div>   |  |                                     | Classification System   | Classification Symbols   | IPC <sup>4</sup>   | C 08 J; C 08 K<br>C 08 L;<br>H 01 Q;   |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| Classification System   | Classification Symbols   |                                     |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| IPC <sup>4</sup>  | C 08 J; C 08 K<br>C 08 L;<br>H 01 Q;   |                                     |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category <sup>9</sup></th> <th style="width: 70%; border-bottom: 1px solid black;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 20%; border-bottom: 1px solid black;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">GB, A, 2058794, (NITTA BERUTO) 15 April 1981,<br/>see claims; page 1, lines 53-85; examples</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1, 2, 7, 10, 12,<br/>26, 29</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="text-align: center; vertical-align: top; padding: 5px;">--</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">CA, A, 1063747 (J.D.L. TESSIER et al.) 2<br/>October 1979,<br/>see claims 1, 4; page 4a - page 5, line 2</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1, 2, 7, 10, 12,<br/>26, 29</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="text-align: center; vertical-align: top; padding: 5px;">--</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">Chemical Abstracts, Volume 89, part 2, 10<br/>July 1978, (Columbus, Ohio, US)<br/>see abstract No. 89=7325F<br/>&amp; JP, A, 7818647 (SUMITOMO ELECTRIC IN-<br/>DUSTRIES)</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-3, 5, 7, 10,<br/>12, 26, 29</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="text-align: center; vertical-align: top; padding: 5px;">--</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">GB, A, 1271298 (CIBA-GEIGY) 19 April 1972,<br/>see claims 1-8; page 2, lines 50-79;<br/>examples I, II; pages 35-124</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="text-align: center; vertical-align: top; padding: 5px;">--</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">FR, A, 2112215 (GRUNZWEIG &amp; HARTMANN) 16 June<br/>1972, see claims 1, 2, 4, 5</td> <td style="text-align: center; vertical-align: top; padding: 5px;">26, 27, 28</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="text-align: center; vertical-align: top; padding: 5px;">--</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0102335 (KEMANORD) 7 March 1984,</td> <td></td> </tr> </table> |  |                                     | Category <sup>9</sup>   | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>   | Relevant to Claim No. <sup>13</sup>                                | A  | GB, A, 2058794, (NITTA BERUTO) 15 April 1981,<br>see claims; page 1, lines 53-85; examples | 1, 2, 7, 10, 12,<br>26, 29 | A | -- |  | A | CA, A, 1063747 (J.D.L. TESSIER et al.) 2<br>October 1979,<br>see claims 1, 4; page 4a - page 5, line 2 | 1, 2, 7, 10, 12,<br>26, 29 | A | -- |  | A | Chemical Abstracts, Volume 89, part 2, 10<br>July 1978, (Columbus, Ohio, US)<br>see abstract No. 89=7325F<br>& JP, A, 7818647 (SUMITOMO ELECTRIC IN-<br>DUSTRIES) | 1-3, 5, 7, 10,<br>12, 26, 29 | A | -- |  | A | GB, A, 1271298 (CIBA-GEIGY) 19 April 1972,<br>see claims 1-8; page 2, lines 50-79;<br>examples I, II; pages 35-124 | 1 | A | -- |  | A | FR, A, 2112215 (GRUNZWEIG & HARTMANN) 16 June<br>1972, see claims 1, 2, 4, 5 | 26, 27, 28 | A | -- |  | A | EP, A, 0102335 (KEMANORD) 7 March 1984, |  |
| Category <sup>9</sup>   | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>   | Relevant to Claim No. <sup>13</sup> |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
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| A   | Chemical Abstracts, Volume 89, part 2, 10<br>July 1978, (Columbus, Ohio, US)<br>see abstract No. 89=7325F<br>& JP, A, 7818647 (SUMITOMO ELECTRIC IN-<br>DUSTRIES)  | 1-3, 5, 7, 10,<br>12, 26, 29        |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
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| A   | GB, A, 1271298 (CIBA-GEIGY) 19 April 1972,<br>see claims 1-8; page 2, lines 50-79;<br>examples I, II; pages 35-124   | 1                                   |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| A   | --   |                                     |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| A   | FR, A, 2112215 (GRUNZWEIG & HARTMANN) 16 June<br>1972, see claims 1, 2, 4, 5   | 26, 27, 28                          |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| A   | --   |                                     |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| A   | EP, A, 0102335 (KEMANORD) 7 March 1984,  |                                     |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> <sup>10</sup> Special categories of cited documents:<br/>           "A" document defining the general state of the art which is not considered to be of particular relevance<br/>           "E" earlier document but published on or after the international filing date<br/>           "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br/>           "O" document referring to an oral disclosure, use, exhibition or other means<br/>           "P" document published prior to the international filing date but later than the priority date claimed         </td> <td style="width: 50%; vertical-align: top; padding: 5px;">           "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br/>           "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<br/>           "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<br/>           "&amp;" document member of the same patent family         </td> </tr> </table>  |  |                                     | <sup>10</sup> Special categories of cited documents:<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier document but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<br>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<br>"&" document member of the same patent family |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| <sup>10</sup> Special categories of cited documents:<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier document but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed   | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<br>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<br>"&" document member of the same patent family |                                     |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| <b>IV. CERTIFICATION</b> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;">           Date of the Actual Completion of the International Search<br/> <b>1th July 1985</b> </td> <td style="width: 50%; vertical-align: top; padding: 5px;">           Date of Mailing of this International Search Report<br/> <b>17 JUL. 1985</b> </td> </tr> <tr> <td style="vertical-align: top; padding: 5px;">           International Searching Authority<br/> <b>EUROPEAN PATENT OFFICE</b> </td> <td style="vertical-align: top; padding: 5px;">           Signature of Authorized Officer<br/> <div style="text-align: right;"> <br/> <b>G.L.M. Kruidenberg</b> </div> </td> </tr> </table>  |  |                                     | Date of the Actual Completion of the International Search<br><b>1th July 1985</b>   | Date of Mailing of this International Search Report<br><b>17 JUL. 1985</b>   | International Searching Authority<br><b>EUROPEAN PATENT OFFICE</b> | Signature of Authorized Officer<br><div style="text-align: right;"> <br/> <b>G.L.M. Kruidenberg</b> </div> |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| Date of the Actual Completion of the International Search<br><b>1th July 1985</b>   | Date of Mailing of this International Search Report<br><b>17 JUL. 1985</b>   |                                     |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |
| International Searching Authority<br><b>EUROPEAN PATENT OFFICE</b>  | Signature of Authorized Officer<br><div style="text-align: right;"> <br/> <b>G.L.M. Kruidenberg</b> </div>   |                                     |   |  |  |  |  |                            |   |    |  |   |  |                            |   |    |  |   |   |                              |   |    |  |   |  |   |   |    |  |   |  |            |   |    |  |   |   |  |

| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) |  |                            |
|--|--|----------------------------|
| Category *   | Citation of Document, with indication, where appropriate, of the relevant passages | Relevant to Claim No       |
|  | see claims<br><br>-----  | 1, 2, 7, 13, 26,<br>29, 30 |

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO.

PCT/US 85/00625 (SA 9453)

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| Patent document<br>cited in search<br>report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|--|---------------------|----------------------------|---------------------|
| GB-A- 2058794                                | 15/04/81            | None                       |                     |
| CA-A- 1063747                                | 02/10/79            | SE-A- 7608086              | 31/01/77            |
| GB-A- 1271298                                | 19/04/72            | DE-A, B, C 1957114         | 11/06/70            |
|  |                     | FR-A- 2030072              | 30/10/70            |
|  |                     | US-A- 3652486              | 28/03/72            |
| FR-A- 2112215                                | 16/06/72            | NL-A- 7103795              | 05/04/72            |
| EP-A- 0102335                                | 07/03/84            | SE-A- 8204595              | 06/02/84            |
|  |                     | JP-A- 59047236             | 16/03/84            |
|  |                     | US-A- 4483889              | 20/11/84            |

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